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Cryogenic Insulation Studies

BY

James M. Stuckey

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CRYOGENIC INSULATION ACTIVITIES
J.M. STUCKEY
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I. CPR-488/141-B PROBLEM (CPR XUS)

In MMC/MAF testing of CPR XUS foams (Lot 1 and 2), they encountered a high number of cryoflex failures. These failures were attributed to one or all of the followings:

- a. Failed to weight down (restrain) panels for 24 hours after spraying (in my opinion this was the most probable cause).
- b. Change in isocyanate index from 300 to 320 -340.
- c. Higher concentration of amine and TIN catalysts than in CPR-488.

Lot 3 had same catalysts level as in CPR-488 and the sprayed panels were restrained. The cryoflex tests results showed marked improvement, but still encountered an occasional failure and increased number of cracks in the foam that did not constitute a failure, but are undesirable.

Elana Blevins (MMC) did a catalyst study for optimization (40°F handmix reactivities and exotherm measurements). The results of these test indicated the catalyst level should be the same as in CPR-488, but the amine catalyst should be reduced approximately 5% and the potassium catalyst concentration increased about 5%. Three sprays of CPR XUS with this new catalyst blend all resulted in good looking foam. The first spray had somewhat thin knit line thickness of 3/8-1/2 inches. Cryoflex tests on foams from these three sprays all passed requirements (CPR XUS catalysts adjusted foam).

Attended meeting with MMC/MAF on November 17, 1993 on the strain capabilities of CPR XUS Lot #2, Lot #3, and Catalyst Adjusted Foams. All three foams had about the same strain capabilities at -423°F (2.12%, 2.09% and 2.14% respectively), but were about 10% lower than CPR-488 (2.38%). All the CPR XUS foams used HCFC 141-B as the blowing agent in place of CFC-11. The final decision was to have Dow make the 4th lot of foam the same as CPR XUS Catalyst Adjusted. A meeting is planned at Dow on December 3, 1993. Based on the results that I have seen, I could not make a firm recommendation for either Lot #3 or catalyst adjusted foam at the present time.

However, it appears as if both formulations would probably be acceptable. Lot #2 is more reactive than the other two foams, and could possibly cause foam tip build up on long duration sprays. At a meeting at Dow, they had no objection to making the catalyst adjustment that Elana Blevins (MMC/MSFC) proposed. The 4th lot of foam was order with this catalyst blend (CPR XUS Catalyst Adjusted). This foam was received at MSFC, and test panels and special test specimens are in the process of being sprayed for qualification testing.

II. CPR XUS FOAM POPCORNING (WIND TUNNEL TEST)

In a Wind Tunnel Test at AEDC, it was reported that CPR XUS Lot #3 foam had popcorned during these tests, and that higher recession rates were encountered. This report was somewhat in error. Kopfinger reported they had always had popcorning with CPR-488. The latest wind tunnel results on CPR-488 had shown slightly higher recession rates than had been obtained earlier. The recession curve was not changed because the rates were very close. The recession rates on CPR XUS Lot #3 foam are essentially the same as the most recent recession rates on CPR-488 except at the lowest heating rates where the recession appears to be slightly higher.

In separation photos on some shuttle flight some slight popcorning has been observed in the CPR-488 foam, particularly above the 2058 ring frame. The ET passes through a region where heating is initiated after the vehicle is exposed to reduced atmospheric pressure. This condition encourages popcorning. It is my opinion that part of the popcorning problem is due to the spraying of the foam panels in the engineering booth at 20-25 lbs per minute as compared to spraying at 40 lbs/min in production and at the booth at MSFC. On this basis I expect the CPR XUS catalyst adjusted foam sprayed at MSFC will show less popcorning than encountered with CPR XUS Lot # 3 foam. I suggested a series of thermal/vacuum test that could have shed some light on the popcorning problems. This suggestion for thermal/vacuum testing was not to well received at MAF.

III. BX-250/141-B SPRAY PROBLEM

With the initial two lot, it was found that they could not consistently pass cryoflex test when the foam was sprayed on metal surfaces that were below 80°F. Often the second coat would complete its rise before the rise of the initial coat was complete. Inspection on foam sprayed on 70°F and 75°F showed a high density foam layer next to the substrate and delamination of the foam layers in some areas of the first knit line. This is believed due to the higher boiling point of 141-B as compared to CFC-11 (~75° vs 90°F).

This problem was apparently overcome by increasing the component temperatures prior to spraying as evidenced by the success obtained with cryoflex with Lots #3 & #4. Unfortunately when Lot #5 was sprayed with higher component temperatures ($125^{\circ}\text{F} \pm 5^{\circ}\text{F}$) on 70°F to 75°F substrates, cryoflex failures were again encountered. Increasing the component temperatures to $135^{\circ}\text{F} \pm 5^{\circ}\text{F}$ did not eliminate cryoflex failures. Receiving inspection did not reveal any major differences in Lots #3, #4, and #5. Lot #5 has a somewhat higher water content than is normally acceptable (0.26% vs max 0.2%). Finger printing revealed a small peak in lot #5 that has not been identified.

There are some possibilities for correcting these deficiencies in the BX-250/141-B foams. One would be to formulate with a more active catalyst. However, this could cause other problems. Another option would be to replace some of the 141-B with R-22, a much lower boiling point HCFC. Our previous data has indicated that about 8% R-22 could be added to the B component of NCFI (no blowing agent) at ambient temperature of 70°F - 75°F . It is believed that no more than 5% R-22 should be added. Based on molar ratio, this would be the equivalent of replacing 6.7% of HCFC 141B. Another possibility might be in controlling spray conditions to obtain a thicker initial spray coat and then delaying the following spray coat to maximum overlap time.

Elana Blevins (MMC) cup reactivity test did not show any major difference between Lot #3 and Lot #5, but both cup reactivity tests did not give acceptable looking foam. The addition of small amount of polycat #5 catalyst improved the looks of the cup foam in the cup reactivity test to a slight extent. It is planned to spray some of the BX-250/141-B material with some Polycat #5 catalyst in "B" component. A meeting with Stephan (vendor for BX-250) is planned to discuss the problem and possible solutions.

NCFI 24-57 (NCFI-141B)

Initial testing of NCFI 24-57 with heated substrate had no cryoflex specimens failure. I was unable to find out whether the specimens had been restrained or not during cool down to room temperature, and no mono-strain data are available. In the 4th spray, it was attempted to heat the substrate by increasing the temperature within the cell (all temperature outside the spray box). Cryoflex failures were encountered at 105°F substrate temperature and at 112°F and 117°F substrate temperature when the RH exceeded 17%. More testing is needed prior to adapting cell external heating of the substrate rather than internal heating of the substrate.

The excellent results obtained so far with NCFI 24-57 is some what surprising. Using CFC-11 blowing agent NCFI 22-65 foam did not have the strain capabilities of CPR-488 foam, and on this basis I would have expected problems with NCFI 24-57.

V. PDL 4034/141B POUR FOAM

MAF is reporting excellent results when HCFC 141B blowing agent replaced the CFC-11 blowing agent in the PDL 4034 pour foam. Realizing that PDL 4034/141-B is a pour foam and there are no knit lines, I would still expect a higher density layer at the substrate when poured on substrates that are colder than 80°F. I have not been able to confirm whether this happens or not.

VI PRIMER FOR ET

MMC is currently having difficulties in finding and qualifying a replacement corrosion resistant primer for the ET. They presently use a chromate filled epoxy primer from DeSoto. Chromates are considered suspect carcinogens and may be restricted in the near future. On the S-II stage of the Saturn V an epoxy phenolic primer was used on the LH2 tank except in the weld land areas. This M-602 primer was obtained from Pittsburg Plate Glass Company, and was useable over a temperature range of -423°F to +300°F. It is not believed to contain chromates since it required a cure of 180 minutes at 290°F. So far I have been unable to find any corrosion data on this material, but Ralph Higgins seem to recall that it wasn't good for corrosion when the primer was nicked or scratched. To improve adhesion of spray foam to the primed surface, a thin coat (0.0005 inches) of a modified polyester/isocyanates adhesive primer from Furnace Plastic (Primer M) was applied over the epoxy phenolic coating.

Scottie Sparks has obtained the North Americal/Rockwell material specification for M-602 primer. He has on order the processing specification for M-602 primer, and also the material and processing specification for the Primer M. The M-602 primer was applied to 2014-T6 aluminum. The primer was required to withstand strains of 0.0044 inches per inch of interface length.

On thinking over the problem of using polymer coatings to protect metal surfaces from corrosion, it was obvious that spray application of solutions of polymers on metal surfaces followed possibly by a post elevated temperature cure was undesirable. This method of application would not eliminate the volatile organic chemical release to the atmosphere problem (currently the most pressing problem) and post elevated temperature cure of the coating on the ET is not very feasible.

On this basis Tim McKechnie of Rocketdyne was approached on the feasibility of applying coatings to metal surfaces by the Flame Spray System, the Plasma Spray System, or other thermally spray methods. If any of these application procedures are ever used on the ET, it will be necessary to control the thickness of the coating, and repair procedures would be required.

For use on the ET, the following 4 requirements have to be met: (1) applied polymers must have acceptable bond strength to the metal surfaces over a temperature range of -423°F to 300°F , (2) the applied polymers on various metal surfaces must have the required strain capability at temperatures as low as -423°F , (3) the surface of the applied polymer must be readily bondable to by spray and pour foams, and possibly adhesives, and (4) the applied polymer must provide corrosion protection to the metal surfaces in thicknesses of 0.5 to 1.5 mils. Less strenuous requirements will be required on the coating for use on the SSME particularly with respects to requirement 1&2.

A presentation was prepared on our proposal to thermally spray an organic coating as a corrosion inhibiting primer on metal surfaces. This proposal was presented to Dr. Patterson, Mr. McIntosh, Mr. Key, Mr. Schuerer and Mr. Pessin. Questions were raised on testing of water-base primers and on the results of testing at MMC/MAF.

At a later meeting on thermally spraying polymer coatings as a primer on metal surfaces, Audrey Landers reported on activities at MAF to find a primer system to replace the currently used primer on the ET. This effort has been primarily on the evaluation of various primer (mostly water base epoxy systems) furnish by a number of paint and coating vendors. Only 2 or 3 vendors showed any interest in working with MMC to overcome problems with their products. The general mode of failure was at cryogenic temperature. Testing of the primers was usually based on bond strength at RT, cryostrain with bonded on SLA at -423°F , corrosion after 1000 hrs on test, and possibly bond test at cryogenic temperatures.

Rocketdyne also prepared a proposal on the same subject for presentation to the Space Shuttle Main Engine Project Office. They proposed trying three methods for thermally spraying polymers on metal surfaces. I attended a meeting where Rocketdyne's proposal was presented to Mike Liberman from Space Shuttle Main Engine Project office.

It was decided to form a joint program of Rocketdyne, Martin Marietta, and MSFC to carry out the program on Thermally Spraying Polymeric Material on Metal Surface as a Corrosion preventive Coating. The program is being jointly funded by ET and SSME program offices.

Rocketdyne is now proposing to evaluate one of the three methods in-house, and use equipment manufacturers to explore the other two methods. The initial effort on evaluating the coatings will be limited to bond strength of the coating to the metal surface, bend test at -320°F, and corrosion tests.

Initial tests will be on 2219 aluminum and stainless steel. They have a quote for the use of a LN₂ cooled ballmill for one day of \$750 to grind resin to powder. The cost per lb of grinding resins will be either \$15.00 or \$7.50 depending on whether 1 or 2 50lb. lots of resin are ballmilled.

I raised a concern on the thermal spray affecting the temper of the 2219-T6 aluminum. Joe Montano gave me a report he issued in march, 1967 where he showed the strength properties of 2219-T87 and 2219-T6 were only affected slightly by exposure to 600°F for 5 minutes.

Information was obtained on a number high temperature thermoplastic polymers that might meet the ET requirements if these resin can be successfully applied by a thermal spray method and are as follows:

1. Thermoplastic Polyimide -Ciba-Geigy Matrimid #5218 (flake form) and Matrimid #9725 (powder form). Scotty Sparks got 200 gms. of Matrimid #5218, and Martin Marietta purchased two pounds of Matrimid #9725.
2. Thermoplastic Polyimide - Furon Advanced Polymers Division, Melden 2001, 3000E, and 6001, all powder. They furnished a few grams of all three types for size distribution analysis by Rocketdyne.
3. Thermoplastic Polyetherimide - General Electric Ultem 1000, Dixon industries produces films from Ultems 1000 in thickness as low as 0.25 mils. Not available as powder.
4. Thermoplastic PEEK Resin - Victrex Peek Grade 150PP unfilled fine powder. EDO Corporation Performance Coating has thermally sprayed this material. However, they reported the coating is extremely brittle.
5. Thermoplastic PBI Resin-HOECHOT Celanese Corporation. This material was of interest to us due to its low coefficient of expansion 13×10^{-6} in/in/°F which is very close to that of aluminum. Unfortunately PBI is not a true thermoplastic and does not flow; hence it does not appear attractive for our application.

6. Thermally Stable Poly(Amide-imide)-AMOCO Corp. This material is a thermal set resin and would require a post cure starting at 200°F and ending at approximately 500°F. The requirements for post cure eliminates it from consideration for the ET.
7. Thermoplastic Polyethersulfone-AMOCO Corp. Radel A-300 is the high flowing grade. The polyethersulfone has a higher water absorption than the polyimide polymer; hence it is less attractive.
8. Thermoplastic Polyphenylene Sulfide -Phillips 66 produces Ryton PPS in a number of different powders. The v-1 powder can be made in a slurry with water and then spray applied onto a metal substrate. The coating requires a min cure of 30 minutes at 700°F. Information I have is not to clear on whether thermally sprayed material might require a post cure.
9. We are still looking for a thermoplastic or thermoset resin that could be more easily sprayed for Rocketdyne use.

It was decided to see if we could apply a coating of the Ciba Geigy thermoplastic polyimide resin #5218 on an aluminum substrate. I suggested we use a combination of three solvents to form the solution. Four potential solvents with boiling points in the 40°C to 105°C range were selected. Scottie Sparks and I dissolved 10 gms of #5218 resin in 40 gms of chloroform by adding the resin slowly to the solvent. It was later diluted with about 44 gms of an approximate 50:50 blend of methylene chloride and 1,2 dichloroethane. This solution was used to paint a clean piece of 2219 aluminum using a very poor paint brush. The solution did not flow readily and dried to a non-uniform coating. The coating dried to tack free in a very few minutes. Later a 5 mil doctor blade was used to coat a film on clean aluminum. The doctor blade was not moved across the surface at a uniform rate, and we ended up with a coating thickness that varied from 1-4-2 mils in thickness. Although we have no actual data on the adhesion of the coating to the aluminum, the coating did stick to the metal.

Later, we replaced the solvent lost from #5218 solution with chloroform and a small quantity of methylene chloride. This solution was used to coat a sample of 0.032" aluminum. The aluminum had been sand blasted leaving a warped panel. The coatings in two areas applied by a 5 mil doctor blade were not uniform due to our inability to hold down the warped panel. After a 2 day cure at about 70°F, a one-inch by eight-inch specimen was cut from the best portion of the two coated areas. These specimens were placed in LN₂ and shown no indication of cracks, or debonding when withdrawn. They were replaced in LN₂, withdrawn, and quickly bent in a 360° curve.

The poorer specimen cracked across the one inch specimen, and debonded in two real thick coating area. Nothing appeared to happen on the best specimen.

A new solution of the #5218 polyimide resin was prepared as described previously. This solution was used to coat a slightly warped 0.032" aluminum panel in two areas using a 5 mil doctor blade. The aluminum panel had been lightly sand blasted and then further clean with scotch brite pads and solvent. The best panel had most of the panel coated with 0.7 to 0.8 mils of polymer; the other panel had a thin coated area with only 0.2 mils of polymer. No tests have been run on these coated panels.

VII. POTENTIAL TMPP TOXIC PROBLEM

There is a very slim potential TMPP toxic problem associated with the experimental foams MMC/MSFC is working with. Foams generally contain a phosphorus flame retardant, hence, the polyol fraction should not contain trimethylol propane or derivative. When the problem came up in 1975, the foam suppliers, excepting Dow, all gave MMC written verification that their foam raw materials did not contain trimethylol propane or derivative and they are obligated to notify MMC if there is any change in their foam formulations. No other actions have been initiated since then. The toxicity problem with CPR-488 has been controlled by limiting the phosphorus content allowed in this products.

Lauri Rando (MMC/MAF) has no test data on detecting trimethylol propane (TMP) in "B" components of foams or in polyol used in foams. She believes that a procedure can be worked out for detecting TMP in polyol based on differences in molecular weight. Caruso believes that he can do the same testing. Hence, any large quantity of polyol, obtained from a vendor that will not give assurance that his product is free of TMP, will probably be tested for TMP.

VIII. MISCELLANEOUS

1. Attended meeting on loss of PDL-4034 foam from Jackpad. Made 2 suggestions for additions to the Jackpad closeouts test plan.
2. Worked with John Sharpe on developing a one page chart for Mr. Schwinghamer on the Development of Environmentally Safe ET Foams (Third Generation Blowing Agents).
3. Helped John Sharpe set up apparatus to determine solubility of HFC-236 ea (1,1,1,2,3,3 Hexafluoropropane B.P. 6°C) in "B" component (no CFC-11) of PDL-4034. Test indicated this material had adequate solubility.

4. Assisted in the blending of HFC-245ca (1,1,2,2,3, Pentafluoropropane B.P. 25.0°C) in "B" component (No CFC-11) of PDL-4034. Test indicate that there may be a problem of getting enough of this blowing agent in the "B" component. However, this appears now to be a minor problem because any needed blowing agent probably can be added to the "A" component.
5. I was assigned the task to find out what MMC/MAF was doing on compatability of HCFC 141-B blowing agent with respect to the elastmers present in the foam processing equipment. This assignment was due to problems encountered by MMC/MSFC with Viton rubber o-rings and bladders. Wayne Richman (504-257-3574 working for Chuck Williams) has taken over compatability testing from Jerry Kline. He is trying to put together the work done by Jerry Kline. He knows of only one problem at the Engineering Spray Booth, and that is an accumulation bladder on the "B" side (possibly Viton rubber). He has not located a compability study made by Allied Signal evaluating HCFC-141B compatibility with various elastomers. He knows of no recommendations by equipment manufactueres on elastomers to use in foam processing equipment when applying foam using HCFC-141B blowing agent.